REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
11-03-2010	Journal Article	

4. TITLE AND SUBTITLE

Bridged Heterocyclium Di-Cationic *closo*-Icosahedral Perfluoroborane, Borane, and Carborane Salts via Aqueous, Open-Air Benchtop Synthesis (Preprint)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
S. Shackelford, J. Boatz, S. Schneider (AFRL/RZSP); J. Belletire, A. Wheaton, B. Wight (ERC); H. Ammon (Univ. of Maryland); D. Peryshkov, S. Strauss (Colorado State Univ.)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
NAVY053Y

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZSP
10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-RZ-ED-JA-2010-090

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-JA-2010-090

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #10106).

13. SUPPLEMENTARY NOTES
For publication in Organic Letters.

14. ABSTRACT

Thirteen unreported bridged triazolium and imidazolium di-cationic salts, that uniquely pair *closo*-icosahedral perfluoroborane $[B_{12}F_{12}]^{2-}$, borane $[B_{12}H_{12}]^{2-}$, or carborane $[CB_{11}H_{12}]^{-}$ anionic species with unsaturated bridged heterocyclium di-cations, were synthesized in water using an open-air benchtop method. This considerably extends the scope of a reported aqueous synthesis of binary $[Heterocyclium]_2[B_{12}H_{12}]$ and $[Heterocyclium][CB_{11}H_{12}]$ salts. Also, the one-step preparation of five new precursor bridged heterocyclium di-cationic di-halide salts using conventional procedures, and in one case a microwave-assisted procedure, is described.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Dr. Scott A. Shackelford
a. REPORT	b. ABSTRACT	c. THIS PAGE	SAR	30	19b. TELEPHONE NUMBER *(include area code)*
Unclassified	**Unclassified**	**Unclassified**			N/A

Bridged Heterocyclium Di-Cationic *closo*-Icosahedral Perfluoroborane, Borane, and Carborane Salts via Aqueous, Open-Air Benchtop Synthesis (Preprint)

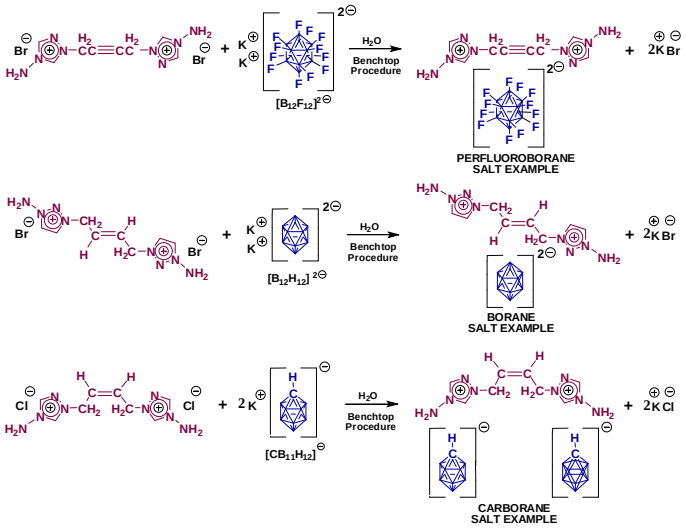
Scott A. Shackelford,* John L. Belletire,† Jerry A. Boatz, Stefan Schneider, Amanda K. Wheaton,† Brett A. Wight,† Herman L. Ammon,‡ Dmitry V. Peryshkov,§ and Steven H. Strauss§

Air Force Research Laboratory, Propellants Branch (AFRL/RZSP), 10 East Saturn Blvd., Edwards AFB, CA 93524-7680, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, and Department of Chemistry, Colorado State University, Fort Collins, CO 80523

scott.shackelford@edwards.af.mil

Received Date (will be automatically inserted after manuscript is accepted)

ABSTRACT



Thirteen unreported bridged triazolium and imidazolium di-cationic salts, that uniquely pair *closo*-icosahedral perfluoroborane $[B_{12}F_{12}]^{2-}$, borane $[B_{12}H_{12}]^{2-}$, or carborane $[CB_{11}H_{12}]^{-}$ anionic species with unsaturated bridged heterocyclium di-cations, were synthesized in water using an open-air benchtop method. This considerably extends the scope of a reported aqueous synthesis of binary [Heterocyclium]$_2$[$B_{12}H_{12}$] and [Heterocyclium][$CB_{11}H_{12}$] salts. Also, the one-step preparation of five new precursor bridged heterocyclium di-cationic di-halide salts using conventional procedures, and in one case a microwave-assisted procedure, is described.

Compared to neutral organic compounds, heterocyclic salts enhance the flexibility to attain rational structural design, and resultant predicted ingredient properties, that can permit a tailorable behavioral response.[1,2] Tailoring thermal initiation of heterocyclium borane and di-nitrate salts to an air-sustained combustion is one example,[2] as is explained by a current initiation sensitivity concept.[3]

We report the first synthesis of heterocyclium perfluoroborane $[B_{12}F_{12}]^{2-}$ salts and the first pairing of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$ anionic species with unsaturated bridged [heterocyclium di-cations]$^{2+}$ in 89-97% yields. The functional unsaturated site centered in the alkyl-based bridge structure, which in turn, possesses a heterocylium cation tethered at each terminal end, is a unique di-cation feature (Scheme 1).

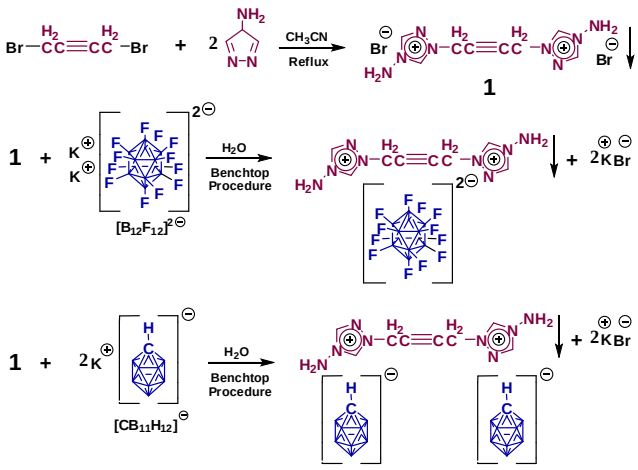
The aqueous, open-air benchtop synthesis of these 13 unique bridged heterocyclium di-cation salts of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$, by a rapid, one-step, high yield metathesis reaction, significantly extends the scope of the recently reported preparation of binary triazolium and imidazolium *closo*-icosahedral borane $[B_{12}H_{12}]^{2-}$ and carborane $[CB_{11}H_{12}]^{-}$ salts in water solvent.[1] An open-air metathesis method for similar binary triazolium and tetrazolium borane-based salts of high water solubility, and for mixed borane salts that pair two different heterocyclium cations in a 1:1 ratio, also is possible.[4] All five precursor bridged heterocyclium di-cation di-halide precursor salts **1-5** (Figure 1) used in this aqueous metathesis reaction were obtained by a one-step alkyation in CH_3CN solvent. Salts **1-4** have no literature precedent.

Two bridged 2-butenyl heterocyclium di-cationic di-halide salts, like salt **5,** have been reported,[5,6] and both contain an N-methylimidazolium cation at the terminal ends of the alkenyl bridge structure. No bridged heterocyclium di-cationic salts based on the 2-butynyl bridge structure or terminal triazolium cations, like salts **1-4**, have been described.

Analogous to the *closo*-icosahedral $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^{-}$ anionic species previously reported,[7-11] and seen in the bridged heterocyclic salts **6-15** (Table 1), the $[B_{12}F_{12}]^{2-}$ di-anion first was synthesized in 1992 as the cesium salt in 38% yield.[12] Recently, the $K_2[B_{12}F_{12}]$ salt was synthesized by $K_2[B_{12}H_{12}]$ perfluorination in 74% yield and 99.5%$^{+}$ purity by continuously bubbling 20/80 F_2/N_2 in CH_3CN solvent using ordinary glassware.[13] Two bridged [heterocyclium][$B_{12}F_{12}$] salts **16** and **17** were synthesized using the $K_2[B_{12}F_{12}]$ reactant salt, while a third **18** was synthesized twice, once with the $Cs_2[B_{12}F_{12}]$ salt (Table 2). The bridged $[B_{12}H_{12}]$, and $[CB_{11}H_{12}]$ salts were synthesized using the $K_2[B_{12}H_{12}]$ and $K[CB_{11}H_{12}]$ reactant salts, respectively, in the correct stoichiometry.[14]

These thirteen 2-alkenyl- and 2-alkynyl-based bridged heterocyclium di-cationic salts of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$ were synthesized in a two-step sequence (Scheme 1). First, five new intermediate bridged heterocyclium di-cationic di-halogen salts **1-5,** needed to prepare the final bridged heterocyclium di-cationic salts **6-18**, precipitated from refluxing CH_3CN solution during a high yield, one-step alkylation of 1,4-dihalo-2-butene or 1,4-dibromo-2-butyne with the selected neutral triazole or imidazole compound (Figure 1). Intermediate salts **1-5**, once filtered and dried, were pure enough for direct use in

Scheme 1. Two-Step Synthesis of Bridged Heterocyclium Di-Cationic Salts of $[B_{12}F_{12}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[CB_{11}H_{12}]^{-}$



the second metathesis step (*e.g.* salt **1**). One intermediate bridged salt **4** (Figure 1) contained 6-7% of unreacted 4-amino-1,2,4-trizole (4AT), but water solvent removed the 4AT impurity during the subsequent metathesis reaction. Reaction times needed to synthesize intermediate bridged di-halide salts **1-5** varied. A typical procedure for salts **1-4** is given by *trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene di-bromide **2**.[15] Synthesis details for salts **1-5** are found in the Supporting Information.

Synthesis of the intermediate bridged heterocyclium di-chloride salt analogue of di-bromide salt **1** was possible using 1,4-di-chloro-2-butyne, but a noticeable amount of the 4-amino-1,2,4-trizole (4AT) reactant (11-16%) remained in the isolated di-chloride salt. Two tedious re-precipitations in a MeOH/CH_3CN mixed solvent, with large losses, removed the 4AT. The availability of 1,4-dibromo-2-butyne, however, provided 4AT-free bridged di-bromide salt **1** in high yield and purity.[16]

Microwave-assisted synthesis reduced alkylation reaction time and gave a comparable yield and purity. Bridged intermediate di-bromide salt **2** was synthesized in 6.5 h conventionally in refluxing CH_3CN (98% yield), but in 50 min at 100 °C under microwave conditions (96% yield). Bridged intermediate salt **5** required 6 h conventionally, but only 45 min at 100 °C in the microwave. A key advantage existed in the synthesis of intermediate bridged salt **3**. While a conventional one-step alkylation yielded acceptably pure bridged salts **1**,**2**,**4**,**5,** intermediate salt **3** was obtained in a 90% crude yield and contained 11% of unreacted 1-amino-1,2,3-triazole (1AT) and other trace impurities. The neutral 1AT heterocycle was removed by re-precipitation from a methanol/ethanol

mixed solvent with an 82% recovery, but the other trace impurities remained. Microwave-assisted synthesis precipitated 1AT-free salt **3** as a pure white solid.

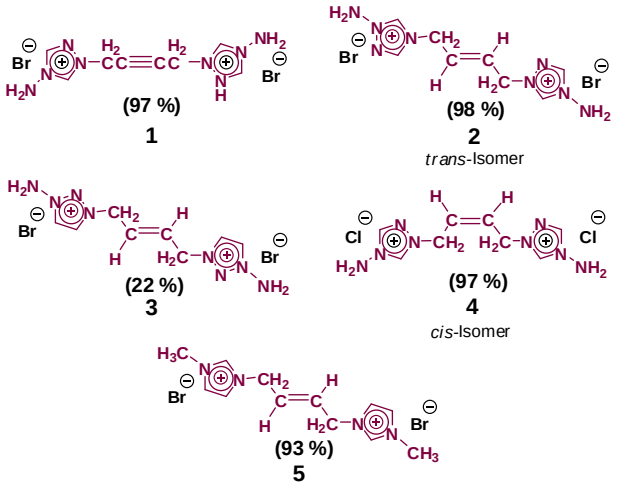


Figure 1. Five Bridged Heterocyclium Di-cationic Di-Halide Reactant Salts Prepared with Yields Obtained.

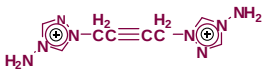
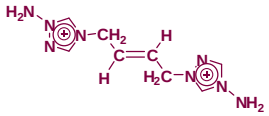
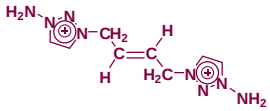
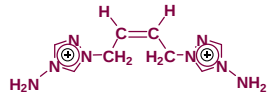
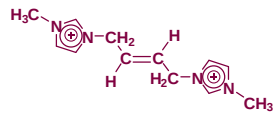
While microwaving the reaction solution in a defined concentration at 100 °C for 45 minutes afforded the best reaction conditions, a 22% yield of precipitated intermediate salt **3** must be an acceptable option.[17,18] A parametric study that increased concentration, increased or decreased reaction time, and increased or decreased temperature, gave either a lower purified yield, or a less pure tan-colored, gummy solid salt **3** which was similar to the conventional alkylation reaction results.

The chemical structure of bridged salts **1-5** demonstrate the flexibilty that these salts provide for systematic structure design to achieve properties modifications that are needed for tailoring chemical performance behavior.[1,2] The unsaturated bond at the bridge center can be varied, the chemical stucture of the tethered heterocyclium cation can be altered, the terminal heterocyclium cations can be changed for another type, and/or the paired anionic species can be exchanged from di-halides to a perfluoroborane, borane, carborane, or a di-nitrate.[2]

A second aqueous, open-air, one-step metathesis reacted intermediate salts **1-5** with either $K_2[B_{12}F_{12}]$, $K_2[B_{12}H_{12}]$, or $K[CB_{11}H_{12}]$ to produce the 13 new bridged heterocyclium di-cation *closo*-icosahedral salts of $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^{-}$ **6-15** (Table 2), and of $[B_{12}F_{12}]^{2-}$ **16-18** (Table 3) as solid precipitates. A typical synthesis procedure is given for the [1,4—di-(4-amino-1,2,4-triazolium-1N)-2-butyne][$B_{12}F_{12}$] salt **18**.[19] Detailed data for salts **6-18** are found in the Supplemental Information.

Initially, smaller scale metatheses (47-320 mg of intermediate bridged salts **1-5**) were conducted at rt by immediately mixing the two aqueous reactants. To minimize the presence of possible KBr or KCl by-product residue, subsequent larger scale aqueous metatheses (849-1550 mg) were run at 78-80 °C by a dropwise addition of aqueous $K_2[B_{12}F_{12}]$, $K_2[B_{12}H_{12}]$, or $K[CB_{11}H_{12}]$ solutions

Table 1. Properties Data for Bridged Heterocyclium Di-Cationic Salts **6-15** of $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^{-}$

UNSATURATED [HETEROCYCLIUM DI-CATION] CHEMICAL STRUCTURE	BORANE $[B_{12}H_{12}]^{2-}$ n = 1	CARBORANE $[CB_{11}H_{12}]^{-}$ n = 2
	Isolated Yield	
	Density (g/cc)	
	Pycnometry (Predicted)	
	Melting/Dec. Point (°C)	
	**6** 93% 1.23 (1.23) dec. 217-219[a]	**7** 92% 1.16 (1.14) dec. 176-178[a]
	**8** 93% 1.21 (1.22) dec. 239-240[a]	**9** 92% 1.16 (1.14) dec. 217-221[a]
	**10** 94% 1.21 (1.25) dec. 230-231[a]	**11** 93% 1.12 (1.16) dec. 230-231[a]
	**12** 92% 1.24 (1.22) dec. 239-240[a]	**13** 93% 1.12 (1.14) melt.. 170-174
	**14** 96% 1.12 (1.25) dec. 305-398[a]	**15** 97% 1.09 (1.16) melt. 252-255

[a] Proceeds with gas evolution

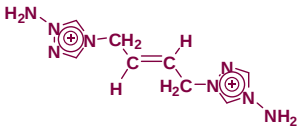
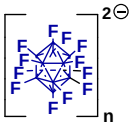
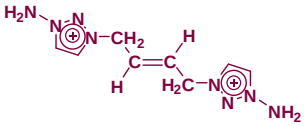
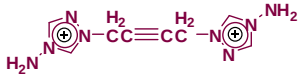
to a solution of salts **1-5**. After precipitation and filtration, the product salt suspension was digested 30 min at 78-80 °C in fresh de-ionized water before final isolation.

Because intermediate bridged heterocyclium di-chloride salt **4** is a clear dark brown glass-like solid with a hard rock candy texture, weighing the exact mass needed for subsequent aqueous metathesis reactions is difficult. Therefore, the amount of salt **4,** needed to synthesize bridged heterocyclium di-cation salts of $[B_{12}H_{12}]^{2-}$ **12** and $[CB_{11}H_{12}]^{-}$ **13,** was prepared individually in two portions.

Isolated yield, density, and melting/decomposition point data for each bridged heterocyclium di-cation borane, carborane, and perfluoroborane salt are listed in Tables 1 and 2. Pycnometry-determined densities at rt and predicted values are compared for salts **6-15** using a newly-developed predictive density additivity code (Table 1).[20] This additivity code predicts an average 3.3%

variance from the 10 pycnometry density values despite two unusually large variances with salts **14** and **15**.

Table 2. Properties Data for Bridged Heterocyclium Di-Cationic Salts **16-18** of $[B_{12}F_{12}]^{2-}$

UNSATURATED [HETEROCYCLIUM DI-CATION] $^{2\oplus}$ CHEMICAL STRUCTURE	$[B_{12}F_{12}]^{2\ominus}$ n = 1	Isolated Yield / Density (g/cc at 23 °C) Single Crystal X-ray at rt / Melting/Dec. Point (°C)
		**16** 98% (small scale) 92% (large scale) 1.73 liquifies 303-304[a]
		**17** 95% (small scale) 1.69 liquifies 238-240[a]
		**18** 93% (small scale) 89% (large scale) 1.72 liquifies 237-238[a]

[a] Proceeds with gas evolution

As expected, bridged [heterocyclium di-cation][$B_{12}F_{12}$] salts **16-18** (Table 2) displayed a single crystal X-ray density at rt that is significantly higher than the analogous bridged [heterocyclium di-cation][$B_{12}H_{12}$] and [heterocyclium di-cation][$CB_{11}H_{12}$]$_2$ salts **6-15** (Table 1). Limited $K_2[B_{12}F_{12}]$ reactant initially dictated that bridged [heterocyclium di-cation][$B_{12}F_{12}$] salts **16-18** be synthesized at rt on a 44-49 mg scale based using reactant salts **1-3**. Bridged salts **16** and **18** later were scaled to 773 and 821 mg, respectively, using the 78-80 °C digestion procedure.[19]

The similar densities for the bridged salts **16-18** result from the formation of planar perpendicular intersecting bridged [heterocyclium di-cation]$^{2+}$ layers that alternate with icosahedral $[B_{12}F_{12}]^{2-}$ di-anion layers (Figure 2). Therefore, the structure of the unsaturated bridged heterocyclium di-cation exerts little effect in altering crystal packing and resultant density values.

Acknowledgement. AFRL/RZ Chief Scientist, Dr. Alan Garscadden, Wright-Patterson AFB, OH, for entrepreneurial research funds. AFRL/RZS, Edwards AFB, CA, for funding and technical support. ERC, Inc., Huntsville, AL, for CSU financial assistance .

Supporting Information Available: Experimental procedures, spectroscopy data, HRMS (all salts), ion chromatography Cl^-/Br^- analyses**,** melting/decomposition points, single crystal X-ray (salts **16-18)**. This material is available free of charge via Internet at http//:pub.acs.org.

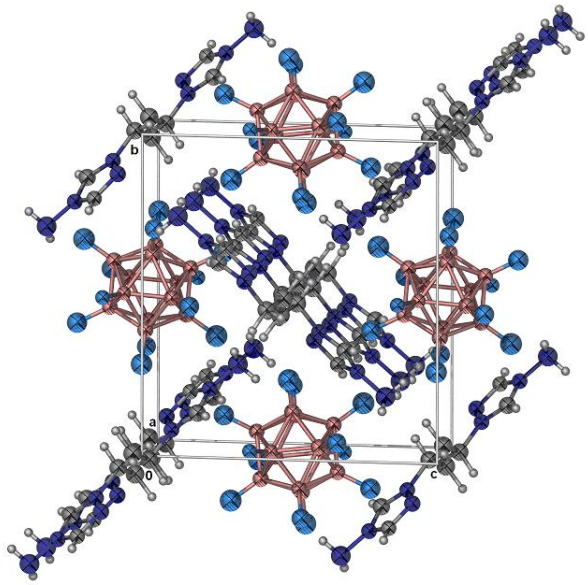


Figure 2. Crystal packing of bridged $[B_{12}F_{12}]$ salt **16** viewed along a slightly tilted crystallographic α-axis.

† ERC, Inc. at AFRL/RZSP, Edwards AFB, CA.
‡ University of Maryland, College Park, MD.
§ Colorado State University, Ft. Collins, CO.

(1) Shackelford, S. A.; Belletire, J. L.; Boatz, J. A.; Schneider, S.; Wheaton, A. K.; Wight, B. A.; Hudgens, L. M.; Ammon, H. L.; Strauss, S. H. *Org. Lett.* **2009**, *11*, 2623.
(2) (a) Shackelford, S. A.; Belletire, J. L. *Centr. Europ. J. Energ. Mater.* **2009**, *6*, 219; (b) Shackelford, S. A.; Belletire, J. L.; 12th New Trends in Research of Energetic Materials (NTREM) Internat. Seminar, Pardubice, Czech Republic, April 1-3, 2009.
(3) Shackelford, S. A. *Centr. Europ. J. Energ. Mater.* **2008**, *5*, 75.
(4) Belletire, J. L.; Shackelford, S. A.; Schneider, S.; Wight, B. A.; Strauss, S. H. *Synthetic Comm*. Submitted for publication.
(5) Zhang, Y.; Ngeow, K. C.; Ying, J. Y. *Org. Lett.* **2007**, *9*, 3495.
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(8) Kaszynski, P. *Collect. Czech. Chem. Commun*. **1999**, *64*, 895, and references therein.
(9) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; M. Dekker: New York, 1969.
(10) Grimes, R. N. *Angew. Chem. Int. Ed*. **2003**, *42*, 1198, and references therein.
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(12) Solntsev, K. A; Mebel, A. M.; Votinova, N. A.; Kuznetsov, N. T.; Charkin, O. P. *Koord. Khim*. **1992**, *18*, 340.
(13) Peryshkov, D. V..; Popov, A. A..; Strauss, S. H. *J. Am. Chem. Soc*. **2009**, *131*, 18393.
(14) The $K_2[B_{12}H_{12}]$ and $K[CB_{11}H_{12}]$ reactant salts were purchased from Katchem Ltd., E. Krasnohorske 6, 110 00 Prague 1, Czech Republic and were used as received.
(15) [*trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][Br]$_2$ (**2**): A 100 mLsingle-necked recovery flask with Teflon®-coated stir bar, was charged with 1.506 g (6.831 mmol) 97% *trans*-1,4-dibromo-2-butene, 1.160 g (13.658 mmol) of 99% 4-amino-1,2,4-triazole, 40 mL CH_3CN and was refluxed 6.5 h. The resultant stirred suspension was cooled to rt, vacuum filtered, and vacuum dried to yield 2.560 g (98%) of white solid salt **2**.

(16) The 1,4-dibromo-2-butyne was purchased from BromOrganics Corporation, P.O. Box 722, Elk Grove, IL 60009.
(17) [*trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene][Br]$_2$ (**3**): Six Biotage (nee *Personal* Chemistry) Initiator Emrys™ 10-20 mL process vials with a coated magnetic stir bar, each was charged with 0.600g (2.72 mmol) 97% *trans*-1,4-di-(1-amino-1,2,3,-triazolium-3N)-2-butene di-bromide, 0.472 g (0.561mmol) 1-amino-1,2,3-triazole,[18] and 20 mL CH_3CN. Each capped vial was microwaved at 100 °C for 45 min, and then, was cooled in a freezer (–13.5 °C). The precipitate in each vial was combined during vacuum filtration. Vacuum drying yielded 0.140 g (22%) of off-white solid salt **3**.
(18) Kaplan, G.; Drake, G.; Tollison, K.; Hall, L.; Hawkins, T. *J. Heterocyclic Chem*. **2005**, *42*,19.
(19) [1,4—di-(4-amino-1,2,4-triazolium)-*trans*-2-butene-1N]$B_{12}F_{12}$] **16**: A 50 mL beaker was charged with a Teflon®-coated magnetic stir bar and 0.773 g (2.02 mmol) of salt **3** which was dissolved in 4 mL DI water. Another 50 mL beaker was charged with 0.865 g (1.98 mmol) $K_2[B_{12}F_{12}]$ that was dissolved in 6 mL DI water. Both beakers were placed on a hot plate that maintained water at 78-80 °C. The water vol was maintained for 15 min by adding DI water as needed. The aq salt **3** solution was stirred vigorously, and the aq $K_2[B_{12}F_{12}]$ occasionally was swirled. The aq $K_2[B_{12}F_{12}]$ solution was added dropwise to the stirred aq solution of salt **3** with a disposable capillary pipette plus 2 x 1mL rinses of the aq $K_2B_{12}F_{12}]$, beaker (9 min total add time). The aq suspension was cooled to rt and placed into a refrigerator (+ 3.0 °C). Vacuum filtration and rinsing the solid cake with 2 x 1 mL pre-chilled (+ 3.0 °C) DI water followed. The semi-dried cake was placed in the same 50 mL beaker with the same stir bar, and 6 mL fresh DI water was added. The stirred suspension was digested at 78-80 °C for 30 min, is cooled to rt and placed into the refrigerator. Vacuum filtration, rinsing the solid cake with 2 x 1 ml pre-chilled DI water, and vacuum drying at rt afforded 1.06 g (92%) of white salt **16**.
(20) Ammon, H. L. *Propellants, Explos., Pyrotech.* **2008**, *33*, 92.

Bridged Heterocyclium Di-Cationic *closo*-Icosahedral Perfluoroborane, Borane, and Carborane Salts via Aqueous, Open-Air Benchtop Synthesis

Scott A. Shackelford,* John L. Belletire,[†] Jerry A. Boatz, Stefan Schneider, Amanda K. Wheaton,[†] Brett A. Wight,[†] Herman L. Ammon,[‡] Dmitry V. Peryshkov,[§] and Steven H. Strauss[§]

Air Force Research Laboratory, Propellants Branch (AFRL/RZSP), 10 East Saturn Blvd., Edwards AFB, CA 93524-7680, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, and Department of Chemistry, Colorado State University, Fort Collins, CO 80523

scott.shackelford@edwards.af.mil

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† ERC, Inc. at AFRL/RZSP, Edwards AFB, CA 93524.

‡ Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.

§ Department of Chemistry, Colorado State University, Ft. Collins, CO 80523.

SUPPLEMENTAL INFORMATION

Table of Contents

References/Notes.

References (1) – (20) appear in the main paper.

(21) See under **X-ray Analyses** section below on this page.

(22) *Handbook of Chemistry and Physics*, 49th ed.; Weast, R. C., Ed.; CRC: Cleveland, OH, 1968. See under Ion Chromatography Results section below (page 23).

General Experimental Comments.

All neutral heterocycles used to synthesize the bridged heterocyclium salts **1-18** were purchased commercially with one exception. The 1-amino-1,2,3-triazole compound was synthesized according to the procedure cited.[18] Deionized (DI) water was obtained from an in-house Millipore MILL-Q Reagent Grade Water System at an 18 megaohm cm purity level. All organic solvents were commercially purchased as either Reagent Grade or HPLC purity, and were used as received.

NMR Analyses. A Bruker Avance 400 Digital NMR instrument was used to obtain both proton (^1H) and ^{13}C spectra.

FTIR Analyses. Fourier transform infrared spectra (FTIR) were taken as powder samples using a Nicolet 6700 Spectrometer in air using with an HATR optical system. Reported are the significant peaks observed.

High Resolution Mass Spectometry Analyses. High resolution mass specta (HRMS) analyses were conducted at UCR Mass Spectrometry Facility, Department of Chemistry, University of California, 501 Big Springs Road (CS1), Riverside, CA 92521, Dr. Richard W. Kondrat, Academic Coordinator, and Mr. Ronald B. New, Staff Research Associate. Analyses were conducted in either the +ev or –ev mode. In all five borane product salts (**2**, **4**, **6**, **8**) and two perfluoroborane salts (**17**, **18**), the Na atom appeared in the resolved salt specta. According to UCR Mass Spectrometry Facility personnel, Na is endemic to the environment, is easily ionized; and therefore, often appears in HRMS results, and the Na seen in several salt products could have come from solvents stored in glass. All seven salts were verified by these HRMS analyses.

Single Crystal X-ray Analyses. The single-crystal X-ray diffraction data were collected on a Bruker 3-circle-platform diffractometer equipped with a SMART APEX 2 detector with the χ-axis fixed at 54.74° and using MoK_α or CuK_α radiation from a fine-focus tube. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. The data collection as well as structure solution and refinement were carried out using standard procedures with the APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, and SHELXTL software packages and programs.[21] Crystal data and refinement details of crystals of **16-18** are given in Table 1-3. Crystallographic data are also available in CIF-format.

(21) APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, SHELXTL ed.; Bruker-AXS, INC.: Madison, WI USA, 2007.

Melting Point Determination. Visually-determined melting point values come from a Stanford Research Systems OptiMelt MPA100-Automated Melting Point Apparatus equipped with digital image video playback software. Observed melting point behavior tends to differ somewhat from what is seen with neutral covalent organic compounds; so, more detail is provided in **Table 4** at the end of this section.

Ion Chromatography Cl^- or Br^- Analysis Results. Ionic Cl^- or Br^- concentrations were determined for product salts (**6-18**), obtained from intermediate di-bromide and di-chloride salts (**1-5**), by Ion Chromatography using a Waters HPLC equipped with a Waters 432 conductivity detector and a Phenomenex STAR-ION A300 100 x 4.6 mm ID (PEEK) analytical column. A Borate/Gluconate eluent was used and system conditions were set according to Waters method #980895.

General Conventional Alkylation Procedure for the Intermediate Bridged Heterocyclium Di-Cation Di-Halide Salt Reactants (1-4).

Either the 1,4-di-halo-2-butene or 1,4-di-halo-2-butyne reagent and the selected neutral triazole or 1-methylimiazole heterocycle were dissolved in Reagent Grade CH_3CN solvent and stirred under reflux using a Teflon®-coated magnetic stirring bar until the precipitated salt product was obtained. Cooling the reaction suspension, vacuum filtration, rinsing the resultant filter cake with several mL of CH_3CN or Et_2O, and drying gave one of the selected bridged heterocyclium di-cation di-halide salts **1-4**. Slight exceptions to the above procedure are noted in the individual salt product descriptions below. In these alkylations,

the millimoles recorded reflect the stated purity of the specific reagent used. The heterocyclium di-cation di-bromide salt **5** was synthesized using a microwave-assisted synthesis procedure.

[*trans*-1,4-di-(1-methylimidazoium)-2-butene-3N][Br]$_2$ (1): A 100 mL 24/40 jointed single-necked recovery flask was charged with 1.500 g (6.803 mmol) of 97% pure trans-1,4-dibromo-2-butene, 1.117 g (13.604 mmol) of 99$^+$% 1-methylimidazole, and 15 mL additional CH_3CN. Refluxing 6 h, cooling in the freezer (–13.5 °C) over the weekend, filtration, rinsing with 4 x 10 mL Et_2O, and drying 24 h at 60 °C on the house vacuum afforded 2.442 g of white salt **3** (95% yield): ^{1}H NMR 400 MHz, std. DMSO-d$_6$ (δ 2.50); δ 9.24 (s, 2H), 7.76 (d, 4H), 6.01-5.99 (m, 2H), 4.91-4,90 (m, 4H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, std. DMSO-d$_6$ (δ 39.51); δ 136.66, 129.02, 123.78, 1.22.34; 49.40, 35.87; FTIR (HATR) cm^{-1}, 3136, 3074, 3043, 2938, 1777, 1675, 1563, 1475, 1409, 1387, 1371, 1335, 1296, 1256, 1159, 1137, 1093, 1074, 984, 956, 890, 846, 792, 754, 652, 616; HRMS calcd for [Cation^{2+} + Br$^-$]$^+$ 297.0709, found 297.0715.

[1,4-di-(4-amino-1,2,4,-triazolium)-2-butyne-1N][Br]$_2$ (2): A 100 mL 24/40 jointed single-necked recovery flask was charged with 2.013 g (9.027 mmol) of 95% pure 1,4-dibromo-2-butyne, 10 mL CH_3CN, 1.502 g (17.685 mmol) of 99% 4-amino-1,2,4-triazole, and 30 mL additional CH_3CN. Refluxing 22 h, cooling for 95 min in the refrigerator, filtration, rinsing with 5 mL pre-chilled (+3.0 °C) in several portions, and drying 22 h at rt under a high vacuum afforded 3.261 g of light tan salt **1** (97% yield): ^{1}H NMR 400 MHz, std. DMSO-d$_6$ (δ 2.50); δ 10.33 (s, 2H), 9.29 (s, 2H), (7.08 (brs, 4H), 5.53 (s, 4H); ^{13}C NMR (100 MHz, std. DMSO-d$_6$ (δ 39.51); δ 145.63, 142.94, 78.88, 41.89; FTIR (HATR) cm^{-1}, 3255, 3116, 3086, 2986, 2948, 2903, 1618, 1562, 1516, 1417, 1359, 1204, 1155, 1070, 995, 884, 771, 645, 609; HRMS calcd for [Cation^{2+} + Br$^-$]$^+$ 299.0363, found 299.0367.

[*trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][Br]$_2$ (3): A 100 mL 24/40 jointed single-necked recovery flask was charged with 1.506 g (6.831 mmol) of 97% pure trans-1,4-dibromo-2-butene, 1.160 g (13.658 mmol) of 99% 4-amino-1,2,4-triazole, and 40 mL CH_3CN. Refluxing 6.5 h, cooling to rt overnight, filtration, rinsing with 3 x 5 mL CH_3CN, and drying 24 h at 60 °C on the house vacuum afforded 2.560 g of white salt **2** (98% yield): ^{1}H NMR 400 MHz, std. DMSO-d$_6$ (δ 2.50); δ10.25 (s, 2H), 9.24 (s, 2H), 7.05 (brs, 4H), 6.08-6.06 (m, 2H), 5.10-5.08 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d$_6$ (δ 39.51); δ 145.38, 142.82, 128.29, 52.44; FTIR (HATR) cm^{-1}, 3254, 3142, 3096, 3041, 2997, 1614, 1583, 1558, 1514, 1439, 1406, 1352, 1326, 1269, 1226, 1207, 1174, 1150, 1071, 1023, 994, 940, 909, 858, 769, 732, 682, 647, 617; HRMS calcd for [Cation^{2+} + Br$^-$]$^+$ 301.0519, found 301.0521.

[*cis*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][Cl]$_2$ (4): A 50 mL 24/40 jointed single-necked recovery flask was charged with 0.590 g (4.480 mmol) of 95% pure cis-1,4-dichloro-2-butene, 15 mL CH_3CN, 0.746 g (8.778 mmol) of 99% 4-amino-1,2,4-triazol (4AT), and another 5 mL CH_3CN. Refluxing 95 h, cooling to rt, and decanting left the dark brown solid stuck to the insides of the reaction flask. Next, 6 mL fresh CH_3CN were added to the reaction flask. Refluxing 6 min, cooling to rt, and decanting the CH_3CN ensued. This CH_3CN reflux trituration was repeated with a 5 min reflux and decanting the solvent to leach out all but 5.6% of unreacted 4AT. Drying 6 days and 17 h, or161 h, at rt under a high vacuum afforded 1.267 g of clear, hard dark brown salt **4** (98% yield incl. 5.6 %

4AT): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ10.46 (s, 2H), 9.26 (s, 2H), 8.86 (s, unreacted 4AT), 7.20 (brs, 4H), 6.05-6.03 (m, 2H), 5.33-5.32 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.24, 143.95 (unreacted 4AT), 142.64, 127.54, 48.42; FTIR (HATR) cm^{-1}, 3179 (sh), 3089, 3015, 1630, 1560, 1409, 1324, 1156, 1070, 1001, 964, 809, 612; HRMS calcd for $[Cation^{2+} + Cl^{-}]^{+}$ 257.1024, found 257.1029.

Note: Regarding assignment of the ^{13}C NMR peak at δ 143.95 as being unreacted 4AT, a smaller reaction scale gave a ^{13}C NMR with three peaks clustered at 145.24 (large), 143.95 (small), 142.64 (large). The 143.95 peak also was suspected to come from 18% unreacted 4AT seen in the proton NMR spectra. Trituration in hot CH_3CN removed most of the unreacted 4AT so that the triturated sample gave ^{13}C NMR peaks only at 145.25 and 142.66 further confirming that the smaller middle peak is unreacted 4AT.

[*trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene][Br]$_2$ (5): Six Biotage (*nee* Personal Microwave) Initiator Emrys™ 10-20 mL process vials containing a coated magnetic stir bar are each are charged with an average of 0.600 g (2.721 mmol) 97% *trans*-1,4-di-(1-amino-1,2,3,-triazolium)-2-butene di-bromide, an average of 0.472 g (5.614 mmol) 1-amino-1,2,3-triazole (1AT),[18] with 20 mL CH_3CN solvent in each reaction vessel. Each reaction vessel was capped/sealed and automatically microwaved at 100 °C for 45 min successively using the reaction vessel transfer feature that is part of the software set-up. The white solid suspension is cooled to rt and is then placed into a freezer (–13.5 °C). The precipitate of each vial is combined during vacuum filtration, and each reaction vessel is successively rinsed with 2 mL pre-chilled (–13.5 °C) CH_3CN which is then filtered through the combined solid cake. The solid cake is then rinsed with 4 mL additional pre-chilled CH_3CN in to portions. Finally, the white cake is rinsed with 5 mL Et_2O and is then dried at 50 °C over the weekend on the house vacuum to yield 0.140 g (22%) of slightly off-white solid salt **5** containing less than 1% unreacted (1AT): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.87 (d, 2H), 8.69 (d, 2H), 8.43 (brs, 4H), 6.18-6.16 (m, 2H), 5.31-5.30 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.91, 128.56, 126.76, 53.35; FTIR (HATR) cm^{-1}, 3171, 3131, 3112, 3083, 3041, 2972, 2961, 2842, 2800, 1622, 1534, 1476, 1426, 1364, 1330, 1234, 1187, 1160, 1079, 1055, 1025, 975, 962, 905, 810, 751, 697, 654, 628; HRMS calcd for $[Cation^{2+} + Br^{-}]^{+}$ 301.0519, found 301.0524.

Larger-Scale General Metathesis Reaction Procedure for Bridged Heterocyclium Di-Cation *closo*-Perfluoroborane, *closo*-Borane, and *closo*-Carborane Salt Products (6-15 and 18).

In order to minimize the presence of residual potassium halide by-product salt, the following general procedure was used for the large scale synthesis runs. An initial aqueous precipitation of the desired product occurred at 78-80 °C, followed by slow cooling to rt, placement in a refrigerator overnight, and isolation of the salt product by filtration. A subsequent aqueous digestion of the isolated precipitated solid product salt was conducted at 78-80 °C, followed by slow cooling, and placement in a refrigerator overnight. Filtration, and final drying in an Electrothermal Chem-Dry® vacuum drying apparatus afforded solid salt products **6-15** and **18**.

A 100 mL beaker, containing with a one-half inch Teflon-Coated magnetic stirring bar, was charged with the selected bridged heterocyclium di-cation di-halide salt (**1**-**5**) which was dissolved at rt in de-ionized (DI) water. A second 100 mL beaker was charged with a nearly stoichiometric amount of potassium *closo*-perfluoroborane, *closo*-borane, or *closo*-carborane which was then dissolved at rt in DI water. Both beakers were then placed for 15 min on a hot plate/stirrer that was calibrated to hold 25 mL DI water at 78 to 80 °C after a 15 min warming time. The beaker with the di-halide reactant salt was stirred while the beaker with the potassium *closo*-borane-based salt was occasionally swirled. Constant volume in both beakers was maintained by use of glass covers and/or by adding DI water as needed. The aqueous potassium borane-based solution was then added dropwise to the stirred aq di-halide reactant salt solution over several minutes duration using a disposable capillary pipette. Immediately or nearly so, precipitation was noted. The spent potassium *closo*-borane-based beaker was rinsed with 2 x 1mL DI water, and each rinse was added to the stirred aqueous suspension in the beaker containing the reaction suspension (Total addition time was from 5 to 17 min, including addition of the DI water rinses, is noted for each product salt). The beaker containing the suspension was covered and allowed to cool to rt before being covered with Parafilm™ and placed in the refrigerator (+3.0 °C) at least overnight. The cold suspension was suction filtered to give a solid cake of the desired product salt, the beaker was rinsed with 2 x 1 mL pre-chilled (+3.0 °C) DI water and each rinse was passed through the solid cake which was air dried of excess water under suction. The semi-dried solid cake was placed back into the same 50 mL beaker with the same stirring bar, and a defined amount of fresh DI water was added to affect a suspension. The stirred suspension was digested on the same hot plate/stirrer in the glass covered 50 mL beaker for 30 min at 78-80 °C to remove any residual potassium halide. The beaker and its contents were cooled to rt; the beaker was covered with Parafilm™, and then, was placed into the refrigerator (3.0 °C) at least overnight. Cold vacuum filtration, rinsing the beaker with 2 x 1 mL pre-chilled DI water, and air drying a defined time gave a semi-dry solid which was transferred to a tarred 4 dram bottle that was subjected to high vacuum drying at 65 °C (50 °C for product salt **9**) to give the final bridged heterocyclium di-cation *closo*-perfluoroborane, borane, or carborane salt product.

[1,4-di-(4-amino-1,2,4-triazolium)-2-butyne-1N][*closo*-$B_{12}H_{12}$] (6): Reacting 1.550 g (4.078 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide (**2)** in 8 mL DI water with 0.879 g (3.996 mmol) of $K_2[B_{12}H_{12}]$ in 12 mL DI water, added over 8 min, gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried for 71 h, gave 1.347 g of a slightly off-white solid product salt **6** (93.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.23 (s, 2H), 9.27 (s, 2H), (7.00 (brs, 4H), 5.50 (s, 4H), 1.30-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.69, 143.01, 78.88, 41.92; FTIR (HATR) cm^{-1}, 3336, 3269, 3118, 3054, 2969, 2936, 2524 (B-H), 2449 (B-H), 1602, 1556, 1523, 1414, 1350, 1272, 1198, 1160, 1061, 1014, 944, 895, 772, 706, 635, 607; HRMS calcd for $[Cation^{2+} + 2Anion^{2-} + Na^+]^-$ 527.5345, found 527.5351.

[1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne][*closo*-$CB_{11}H_{12}$] (7): Reacting 1.450 g (3.815 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide (**2)** in 7 mL DI water with 1.362 g (7.477 mmol) of $K[CB_{11}H_{12}]$ in 7 mL DI water, added over 6 min, gave a solid product salt. [Note: Care must be taken to ensure thorough mixing is acheived with this reaction.] Digestion of the solid product salt with 7 mL fresh DI water, when dried

for 71 h, gave 1.736 g of a light brown solid product salt **7** (91.7 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.24 (s, 2H), 9.27 (s, 2H), (7.01 (brs, 4H), 5.49 (s, 4H), 2.38 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.68, 143.02, 78.87, 50.71, 41.90; FTIR (HATR) cm^{-1}, 3352, 3278, 3239, 3135, 3093, 2980, 2946, 2559 (B-H), 2520 (B-H), 1626, 1426, 1414, 1354, 1171, 1141, 1090, 1023, 999, 931, 894, 860, 840, 758, 717, 687, 638, 609; HRMS calcd for $[Cation^{2+} + Anion^{-}]^{+}$ 363.3215, found 363.3214.

[*trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$B_{12}H_{12}$] (8): Reacting 1.438 g (3.763 mmol) of *trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide (**3)** in 9 mL DI water with 0.827 g (3.759 mmol) of $K_2[B_{12}H_{12}]$ in 12 mL DI water, added over 10 min, gave a solid product salt. Digestion of the solid product salt with 10 mL fresh DI water, when dried for 90 h, gave 1.272 g of a white solid product salt **8** (92.9 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.13 (s, 2H), 9.22 (s, 2H), (6.96 (brs, 4H), 6.06-6.05 (m, 2H), 5.07-5.06 (m, 4H), 1.32-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.45, 142.88, 128.28, 52.52; FTIR (HATR) cm^{-1}, 3332, 3266, 3120, 3051, 2967, 2517 (B-H), 2464 (B-H), 2444 (B-H), 1604, 1556, 1521, 1422, 1360, 1187, 1157, 1060, 1017, 982, 957, 894, 770, 707, 612; HRMS calcd for $[Cation^{2+} + 2Anion^{2-} + Na^{+}]^{-}$ 529.5501, found 529.5484.

[*trans*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$CB_{11}H_{12}$] (9): Reacting 1.031 g (2.698 mmol) of *trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide (**3)** in 7 mL DI water with 0.982 g (5.391 mmol) of $K[CB_{11}H_{12}]$ in 6 mL DI water, added over 7 min, gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried for 75 h at 50 °C, gave 1.262 g of a white solid product salt **9** (92.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.14 (s, 2H), 9.22 (s, 2H), (6.98 (brs, 4H), 6.06-6.05 (m, 2H), 5.06-5.05 (m, 4H), 2.38 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.41, 142.84, 128.31, 52.50, 50.76; FTIR (HATR) cm^{-1}, 3346, 3282, 3240, 3131, 3089, 2547(B-H), 2510 (B-H), 1707, 1625, 1558, 1434, 1361, 1312, 1150, 1149, 1088, 1066, 1022, 979, 922, 864, 765, 714, 608; HRMS calcd for $[Cation^{2+} + Anion^{-}]^{+}$ 365.3371, found 365.3382.

[*cis*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$B_{12}H_{12}$] (10): Reacting 1.256 g (4.286 mmol) of *cis*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide (**4)** in 3 mL DI water with 0.848 g (3.856 mmol) of $K_2[B_{12}H_{12}]$ in 14 mL DI water, added over 17 min, gave a solid product salt. Digestion of the solid product salt with 5 mL fresh DI water, when dried for 96 h, gave 1.299 g of a light brown solid product salt **10** (92.5 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.15 (s, 2H), 9.22 (s, 2H), (6.97 (brs, 4H), 6.04-6.02 (m, 2H), 5.24-5.23 (m, 4H), 1.30-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.36, 142.80, 127.38, 48.62; FTIR (HATR) cm^{-1}, 3337, 3316, 3306, 3213, 3123, 3070, 3003, 2467 (B-H), 2442 (B-H), 1613, 1564, 1532, 1436, 1406, 1323, 1164, 1057, 1006, 960, 950, 867, 806, 711, 651, 637, 605; HRMS calcd for $[Cation^{2+} + 2Anion^{2-} + Na^{+}]^{-}$ 529.5501, found 529.5493.

[*cis*-1,4-di-(4-amino-1,2,4,-triazolium-1N)-2-butene][*closo*-$CB_{11}H_{12}$] (11): Reacting 0.849 g (2.896 mmol) of *cis*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene di-bromide (**4)** in 4 mL DI water with 0.949 g (5.211 mmol) of $K[CB_{11}H_{12}]$ in 6 mL DI water, added over 5 min, gave a solid product salt. [Note: Initially, oil droplets formed, but as more potassium

carborane solution was added, the brown oil solidified to a precipitate.] Digestion of the solid product salt with 7 mL fresh DI water, when dried for 96 h, gave 1.233 g of a light brown solid product salt **11** (93.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.16 (s, 2H), 9.23 (s, 2H), (6.99 (brs, 4H), 6.04-6.02 (m, 2H), 5.23-5.22 (m, 4H), 2.38 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.33, 142.79, 127.41, 50.71, 48.56; FTIR (HATR) cm^{-1}, 3355, 3288, 3248, 3135, 3099, 2537 (B-H), 1637, 1466, 1443, 1403, 1325, 1149, 1088, 1021, 891, 836, 713, 649; 610 HRMS calcd for [Cation^{2+} + Anion^{-}]$^{+}$ 365.3371, found 365.3382.

[*trans*-1,4-di-(1-amino-1,2,3,-triazolium-3N)-2-butene][*closo*-$B_{12}H_{12}$] (12): Reacting 1.329 g (3.478 mmol) of *trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene di-bromide (**5)** in 7 mL DI water with 0.765 g (3.478 mmol) of $K_2[B_{12}H_{12}]$ in 8 mL DI water, added over 9 min, gave a solid product salt. Digestion of the solid product salt with 6 mL fresh DI water, when dried for 96 h, gave 1.192 g of a white solid product salt **8** (94.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.80-8.79 (d, 2H), 8.66 (d, 2H), 8.37 (brs, 4H), 6.17-6.16 (m, 2H), 5.29-5.28 (m, 4H), 1.30-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.93, 128.57, 126.83, 53.42; FTIR (HATR) cm^{-1}, 3324, 3255, 3174, 3128, 3041, 2980, 2942, 2475 (B-H), 2455 (B-H), 2438 (B-H), 1599, 1523, 1473, 1411, 1341, 1248, 1210, 1187, 1088, 1060, 971, 926, 791, 753, 708, 652, 620; HRMS calcd for [Cation^{2+} + 2Anion^{2-} + Na^{+}]$^{-}$ 528.5538 found 528.5549.

[*trans*-1,4-di-(1-amino-1,2,3,-triazolium-3N)-2-butene][*closo*-$CB_{11}H_{12}$] (13): Reacting 1.356 g (3.549 mmol) of *trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene di-bromide (**5)** in 7 mL DI water with 1.293 g (7.100 mmol) of $K[CB_{11}H_{12}]$ in 7 mL DI water, added over 8 min, gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried for 96 h, gave 1.760 g of a cream-colored solid product salt **13** (97.5 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.80 (d, 2H), 8.66-8.65 (d, 2H), 8.38 (brs, 4H), 6.16-6.15 (m, 2H), 5.28-5.27 (m, 4H), 2.39 (brs, 2H), 2.11-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.94, 128.57, 126.79, 53.41, 50.71; FTIR (HATR) cm^{-1}, 3338, 3266, 3146, 3132, 3090, 2998, 2529 (B-H), 1523, 1196, 1167, 1087, 1022, 968, 901, 786, 759, 717, 651; HRMS calcd for [Cation^{2+} + Anion^{-}]$^{+}$ 365.3371, found 365.3374.

[*trans*-1,4-di-(1-methylimidazolium-3N)-2-butene][*closo*-$B_{12}H_{12}$] (14): Reacting 1.437 g (3.802 mmol) of *trans*-1,4-di-(1-methylimidazolium-3N)-2-butene di-bromide (**1)** in 5 mL DI water with 0.823 g (3.762 mmol) of $K_2[B_{12}H_{12}]$ in 10 mL DI water, added over 9 min gave a solid product salt. Digestion of the solid product salt with 10 mL fresh DI water, when dried for 89.5 h, gave 1.307 g of a white solid product salt **14** (96.4 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 9.07 (s, 2H), 7.74-7.73 (m, 2H), 7.70-7.69 (m, 2H), 5.98-5.97 (m, 2H), 4.88-4.87 (m, 4H), 3.86 (s, 6H), 1.31-0.38 (very brm, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 136.61, 129.00, 123.84, 122.32, 49.44, 35.89; FTIR (HATR) cm^{-1}, 3146, 3108, 3030, 2943, 2828, 2475 (B-H), 2452 (B-H), 2435 (B-H), 1723, 1678, 1618, 1574, 1557, 1452, 1368, 1333, 1295, 1266, 1190 1155, 1066, 974, 838, 752, 720, 656, 620; HRMS calcd for [Cation^{2+} + 2Anion^{2-} + Na^{+}]$^{-}$ 525.5691 found 525.5708.

[*trans*-1,4-di-(1-methylimidazolium-3N)-2-butene][*closo*-$CB_{11}H_{12}$] (15): Reacting 1.029 g (2.720 mmol) of *trans*-1,4-di-(1-methylimidazolium-3N)-2-butene di-bromide (**1**) in 4 mL DI water with 0.990 g (5.438 mmol) of K[$CB_{11}H_{12}$] in 6 mL DI water, added over 10 min gave a solid product salt. Digestion of the solid product salt with 7 mL fresh DI water, when dried for 69.5 h, gave 1.332g of a white solid product salt **15** (97.1 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 9.08 (s, 2H), 7.74-7.73 (m, 2H), 7.70-7.69 (m, 4H), 5.97-5.96 (m, 2H), 4.87-4.86 (m, 4H), 3.86 (s, 6H), 2.39 (brs, 2H), 2.08-0.90 (very brm, 22H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 136.63, 129.01, 123.85, 122.31, 49.43, 35.86; FTIR (HATR) cm^{-1}, 3281, 3235, 3162, 3147, 3102, 2537 (B-H), 1595, 1565, 1444, 1384, 1358, 1334, 1295, 1159, 1087, 1021, 980, 890, 827, 739, 716, 617; HRMS calcd for [$Cation^{2+}$ + $Anion^{-}$]$^{+}$ 361.3561, found 361.3577.

[*trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene][*closo*-$B_{12}F_{12}$] (16): Reacting 0.773 g (2.024 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-*trans*-2-butene di-bromide (**3**) in 4 mL DI water with 0.865 g (1.984 mmol) of $K_2[B_{12}H_{12}]$ in 6 mL DI water, added over 9 min, gave a solid product salt. Digestion of the solid product salt with 6 mL fresh DI water, when dried under a high vacuum line for 72 h at rt, gave 1.058 g of a white solid product salt **16** (92.0 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.14 (s, 2H), 9.22 (s, 2H), (6.97 (brs, 4H), 6.06-6.05 (m, 2H), 5.06-5.05 (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.40, 142.83, 128.30, 52.94; FTIR (HATR) cm^{-1}, 3393, 3321, 3150, 3107, 3009, 2975, 1620, 1560, 1440, 1371, 1221 (B-F), 1149, 1072, 1003, 971, 935, 875, 723, 640, 612; HRMS (from smaller scale sample shown below) calcd for [$Cation^{2+}$ - H^{+}]$^{+}$ 221.1263, found 221.1258 in positive mode, and HRMS calcd for [$Cation^{2+}$ + $Anion^{2-}$ - H^{+}]$^{-}$ 579.2266, found 579.2284 in the negative mode.

[1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne-1N][*closo*-$B_{12}F_{12}$] (18): Reacting 0.821 g (2.159 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide (**2**) in 4 mL DI water with 0.922 g (2.115 mmol) of $K_2[B_{12}H_{12}]$ in 11 mL DI water, added over 9 min, gave a solid product salt. Digestion of the solid product salt with 5 mL fresh DI water, when dried for 38 h at rt, gave 1.084 g of a cream-colored solid product salt **18** (88.7 % yield): ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.24 (s, 2H), 9.26 (s, 2H), (7.01 (brs, 4H), 5.49 (s, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.65, 142.99, 78.84, 41.88; FTIR (HATR) cm^{-1}, 3372, 3309, 3149, 3107, 3013, 2985, 2966, 1630, 1568, 1429, 1361, 1219 (B-F), 1074, 1002, 957, 886, 724, 650, 612; HRMS calcd for [$Cation^{2+}$ + $Anion^{2-}$ – H^{+}]$^{-}$ 577.2110, found 577.2093.

Smaller-Scale General Metathesis Reaction Procedure and X-ray Data for Bridged Heterocyclium Di-Cation *closo*-Perfluoroborane Salt Products (16-18). Because of the limited supply of $K_2[B_{12}F_{12}]$ and $Cs_2[B_{12}F_{12}]$ reactant salts, the [Heterocyclium di-cation][$B_{12}F_{12}$] salts initially were synthesized on a smaller reaction scale at rt with no digestion of the initial product salt. These three perfluoroborane salts are very soluble in CH_3CN at rt; so, this solvent was used to obtain crystals suitable for single-crystal X-ray analyses shown below.

A 10 mL 14/20 jointed single-neck recovery flask was charged with the selected bridged heterocyclium di-cation di-halide salt (**2**, **3**, or **5**) which was dissolved at rt in de-ionized (DI)

water. A 50 mL beaker was charged with a nearly stoichiometric amount of potassium *closo*-perfluoroborane or cesium *closo*-perfluoroborane which was then dissolved at rt in DI water. The aqueous potassium or cesium perfluoroborane solution was added dropwise, using a disposable capillary pipette, to the aqueous solution in the 10 mL single-necked recovery flask, and a precipitate immediately began to form. During addition, the flask occasionally was swirled. After complete addition, the beaker was rinsed with 0.4 to 1 mL DI water in two portions which was added to the 10 ml recovery flask. The capped 10 mL recovery flask and its contents were placed overnight in a refrigerator (+3.0 °C). Vacuum filtration, rinsing the 10 mL recovery flask with 1 (salt **16**), 2 (salt **17**), or 3 (salt **18**) mL of DI water, in two, two, and three portions, respectively, passing the rinses through the solid cake in the filtration funnel, and drying the resultant solid cake for at least 18 h at 75 °C in a vacuum oven gave the desired product salt.

[*trans*-1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butene][*closo*-$B_{12}F_{12}$] (16): Reacting 0.0443 g (0.1159 mmol) of 1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne di-bromide (**3)** in 0.6 mL DI water with 0.0500 g (0.1147mmol) of $K_2[B_{12}H_{12}]$ in 0.6 mL DI water, added over less than one min, to give 0.0649 g (97.6%) of solid product salt **16**: ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.14 (s, 2H), 9.22 (s, 2H), (6.98 (s, 4H), 6.06-6.05 (m, 2H), 5.06-5.05, (m, 4H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.39, 142.82, 128.29, 52.48; FTIR (HATR) cm^{-1}, 3391, 3322, 3150, 3097, 3003, 1622, 1556, 1438, 1372, 1221 (B-F), 1148, 1017, 1005, 972, 935, 874, 723, 641, 612; HRMS calcd for $[Cation^{2+} - H^+]^+$ 221.1263, found 221.1258 in positive mode, and HRMS calcd for $[Cation^{2+} + Anion^{2-} - H^+]^-$ 579.2266, found 579.2284 in the negative mode.

Recystallization from CH_3CN to a very concentrated sample permitted single-crystal X-ray analysis. Recrystallization from DI water also gave acceptable X-ray crystals: 23.3 mg of salt **16** was dissolved in 20 mL boiling DI water. Filtration, cooling to rt, very slow air evaporation and concentration of the solution to 5 mL, removal of excess water solvent with a disposable capillary pipette, and slow air drying of the resultant crystals gave 20.4 mg of salt **16** for use in single-crystal X-ray analysis.

Table 1. Crystal and structure refinement data for **16.**

	(16) $(4AT)_2C_4H_6\ B_{12}F_{12}$
Formula	C8 H14 N8, B12 F12
Space group	$P2_1/c$ monoclinic
a (Å)	8.220(1)
b (Å)	12.027(1)
c (Å)	11.690(1)
β (°)	105.839(1)
V/Å^3	1111.87(16)
$\rho_{calc.}$/g cm^{-3}	1.73
Z	2
Formula weight	579.99
μ/mm^{-1}	0.172
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.1x0.2x0.2
Theta range θ/°	2.48 to 28.64
Index range	-10≤h≤10, -15≤k≤15, -15≤l≤15
Reflection collected	13074
Independent [R(int)]/	2700 [0.0286]
Obs. refl. ([I > 2.0 σ(I)])	1823
F(000)	572
GooF	1.069
R_1, wR [I > 2σ(I)]	0.0483, 0.1388
R_1, wR_2 (all data)	0.0726, 0.1559
L.diff. peak/hole eÅ^3	0.28 and -0.21
Absorption correct.	multiscan SADABS
T_{min}, T_{max}	0.662, 0.746
Data/restraints/param.	2700/0/193
Refinement method	Full-matrix least squares on F^2

$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{½}$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

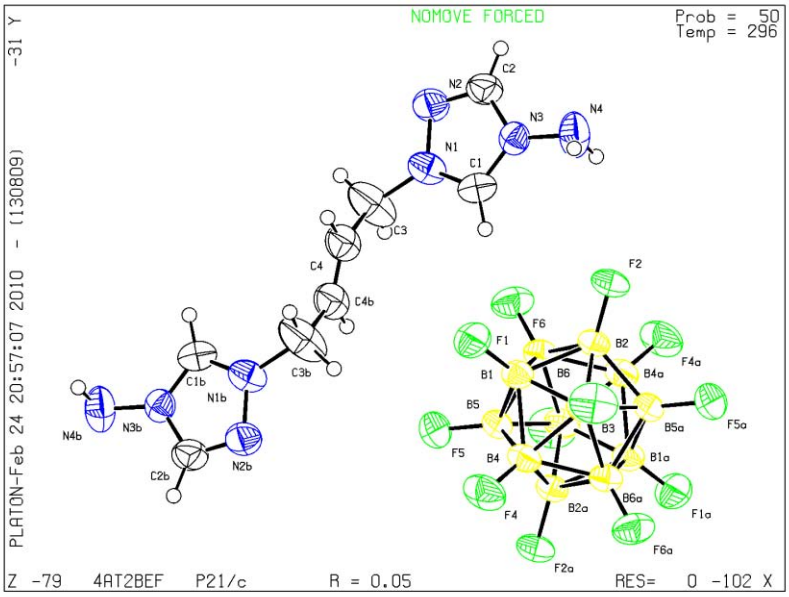


Figure 1. Molecular drawing of **16**. Thermal ellipsoids are shown at 50% probability level.

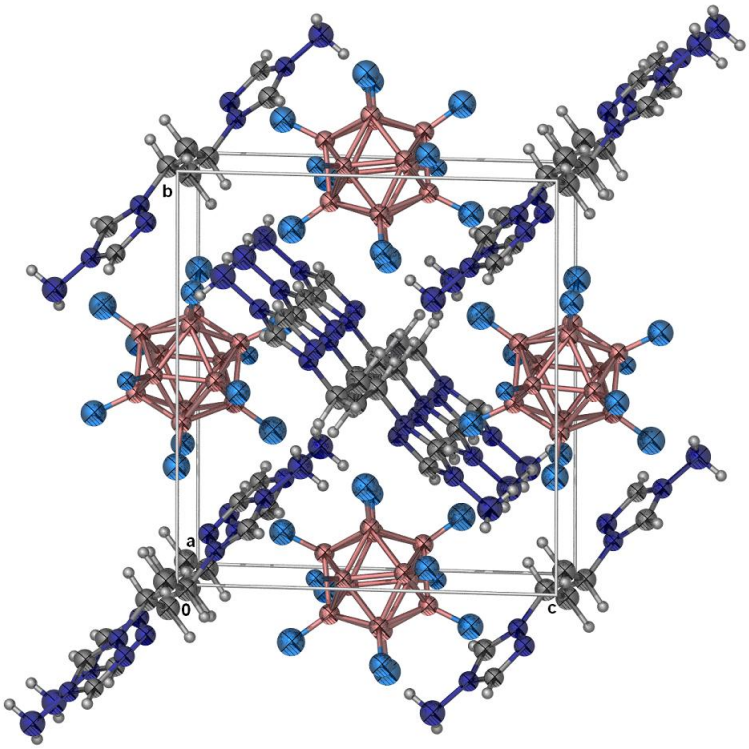


Figure 2. Crystal packing of **16** viewed along the *a*-axis (tiltel forward)

[*trans*-1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butene][*closo*-$B_{12}F_{12}$] (17): Reacting 0.0490 g (0.1282 mmol) of 1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butyne di-bromide (**5)** in 0.6 mL DI water with 0.0539 g (0.1236mmol) of $K_2[B_{12}H_{12}]$ in 0.6 mL DI water, added over less than one min, to give 0.0679 g (94.7%) of solid product salt **17**: ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 8.79 (d, 2H), 8.65 (d, 2H), (8.38 (brs, 4H), 6.16-6.14 (m, 2H), 5.28-5.26, (m, 4H);^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 130.91, 128.56, 126.79, 53.40; FTIR (HATR) cm^{-1}, 3386, 3311, 3189, 3174, 1623, 1530, 1476, 1414, 1357, 1330, 1222 (B-F), 1087, 980, 904, 790, 726, 659, 628; HRMS calcd for $[Cation^{2+} + Anion^{2-} - H^+]^-$ 579.2266, found 579.2246.

Dissolving crude salt product **17** in CH_3CN and evaporating to dryness gives crystals suitable for single-crystal X-ray analysis.

Table 2. Crystal and structure refinement data for **17.**

	(17) $(1AT)_2C_4H_4$ $B_{12}F_{12}$
Formula	B12 F12, C8 H14 N8
Space group	$P2_1/n$ monoclinic
a (Å)	8.318(1)
b (Å)	13.311(1)
c (Å)	10.994(1)
β (°)	110.847(1)
V/Å^3	1137.55(5)
$\rho_{calc.}$/g cm^{-3}	1.69
Z	2
Formula weight	579.99
μ/mm^{-1}	0.168
Temperature (K)	296(2)
λ(MoKα)	0.71073
Crystal size	0.1x0.1x0.2
Theta range θ/°	2.50 to 25.46
Index range	-10≤h≤10, -16≤k≤16, -13≤l≤13
Reflection collected	21415
Independent [R(int)]/	2099 [0.0359]
Obs. refl. ([I > 2.0 σ(I)])	1600
F(000)	572
GooF	1.041
R_1, wR [I > 2σ(I)]	0.0385, 0.1023
R_1, wR_2 (all data)	0.0539, 0.1129
L.diff. peak/hole eÅ^3	0.27 and -0.19
Absorption correct.	multiscan SADABS
T_{min}, T_{max}	0.702, 0.745
Data/restraints/param.	2099/398/289
Refinement method	Full-matrix least squares on F^2

$R_1 = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{½}$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

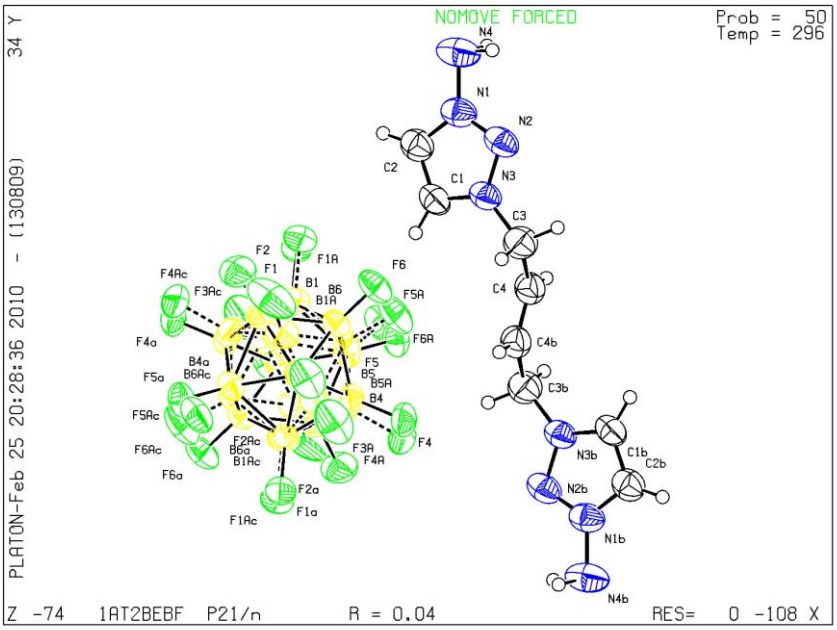


Figure 3. Molecular drawing of **17**. Thermal ellipsoids are shown at 50% probability level ($B_{12}F_{12}^{2-}$ anion is disordered).

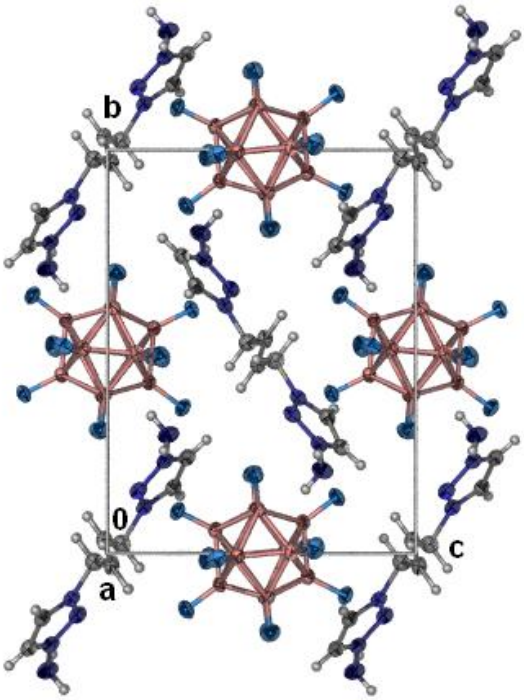


Figure 4. Crystal packing of **17** viewed along the *a*-axis (disorder removed for clarity).

[1,4-di-(4-amino-1,2,4-triazolium-1N)-2-butyne][*closo*-$B_{12}F_{12}$] (18): Reacting 0.1084 g (0.2852 mmol) of 1,4-di-(1-amino-1,2,3-triazolium-3N)-2-butyne di-bromide (**5)** in 0.4 mL DI water with 0.1774 g (0.2845 mmol) of $Cs_2[B_{12}F_{12}]$ in 5 mL (minimum amount needed) DI water, added over a couple of minutes, to give 0.1524 g (92.7%) of cream-colored solid product salt **18**: ^{1}H NMR 400 MHz, std. DMSO-d_6 (δ 2.50); δ 10.24 (s, 2H), 9.27 (s, 2H), (7.01 (s, 4H), 5.49, (s, 4H);^{13}C NMR (100 MHz, std. DMSO-d_6 (δ 39.51); δ 145.66, 142.99, 78.85, 41.88; FTIR (HATR) cm^{-1}, 3375, 3308, 3151, 3107, 2985, 2966, 1631, 1570, 1430, 1363, 1218 (B-F), 959, 887, 725, 716, 652, 613; HRMS calcd for $[Cation^{2+} + Anion^{2-} - H^{+}]^{-}$ 577.2110, found 577.2093.

Dissolving crude salt product **18** in CH_3CN and evaporating to dryness gives crystals suitable for single-crystal X-ray analysis.

Table 3. Crystal and structure refinement data for **18**

	(18) $(1AT)_2C_4H_6\ B_{12}F_{12}$
Formula	C8 H12 N8, B12 F12
Space group	*P*bca orthorhombic
a (Å)	17.066(1)
b (Å)	14.648(1)
c (Å)	17.812(1)
α,β,γ (°)	90
V/Å^3	4452.7(6)
$\rho_{calc.}$/g cm^{-3}	1.72
Z	8
Formula weight	577.98
μ/mm^{-1}	1.542
Temperature (K)	296(2)
λ(CuKα)	1.54178
Crystal size	0.1x0.1x0.2
Theta range θ/°	4.69 to 65.21
Index range	-20≤h≤16, -16≤k≤14, -13≤l≤20
Reflection collected	15709
Independent [R(int)]/	3670 [0.0241]
Obs. refl. ([I > 2.0 σ(I)])	2768
F(000)	2272
GooF	1.048
R_1, wR [I > 2σ(I)]	0.0468, 0.1313
R_1, wR_2 (all data)	0.0630, 0.1444
L.diff. peak/hole eÅ^{-3}	0.36 and -0.37

Absorption correct.	multiscan SADABS
T_{min}, T_{max}	0.643, 0.753
Data/restraints/param.	3670/0/377
Refinement method	Full-matrix least squares on F^2

$R_1 = \Sigma \, ||F_o| - |F_c|| / \Sigma |F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma(w(|F_o|^2)^2)\}^{½}$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

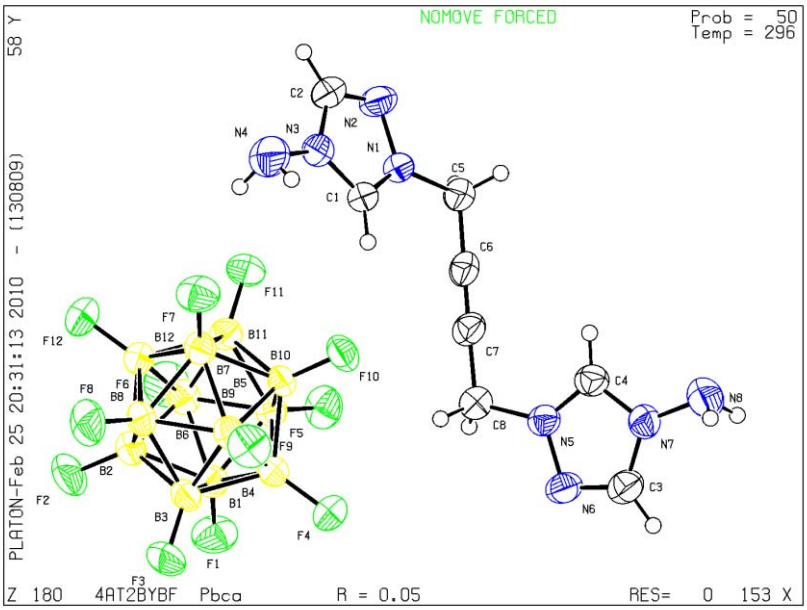


Figure 5. Molecular drawing of **18**. Thermal ellipsoids are shown at 50% probability level.

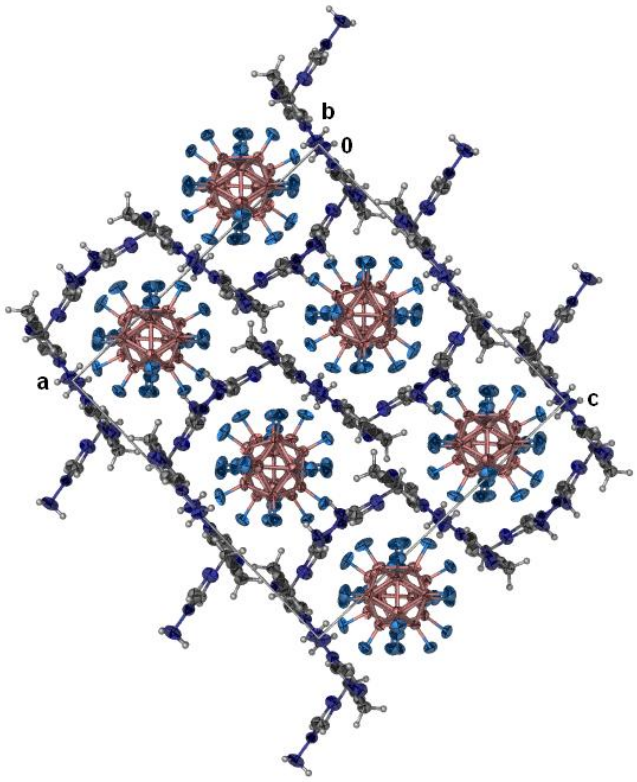


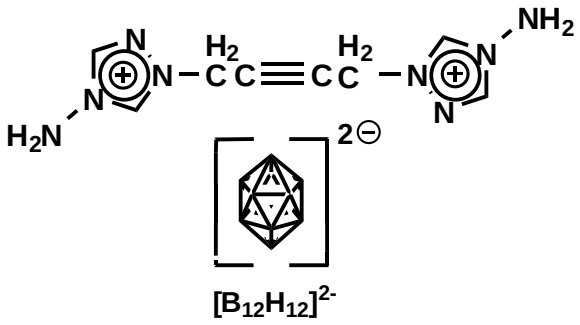
Figure 6. Crystal packing of **18** viewed along the *b*-axis.

Melting Point Data.

Detailed visual melting point behavior for all product salts (**5–18**) is presented in Supplemental Table 1. These values were determined as follows. First, a run was made at a 10 ^{o}C/minute temperature rise to obtain an approximate melting point value for each salt sample; then, a second run was made with each salt sample using a 1 ^{o}C/minute temperature rise beginning about 10 ^{o}C below the initial melt response.

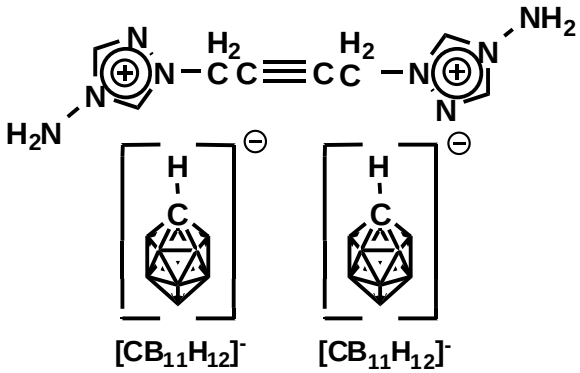
This second run data was used to establish the published melting point or decomposition temperature values (**Table 4**) from iteratively comparing visual observations of each sample directly in the apparatus melting point compartment and the resultant video replay of that same sample. Softening means that the crystalline salt appeared to lose its sharp crystalline character to a more velvet-like solid that was devoid of sharp corners on the solid particles.

Table 4. Melting Point Data Determined with the SRS MPA100 Apparatus.



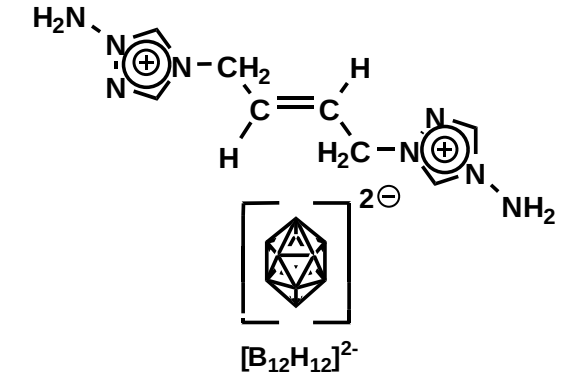
6

DECOMPOSES with solid state gas evolution to a dark residue: 217.4 - 219.6 ºC



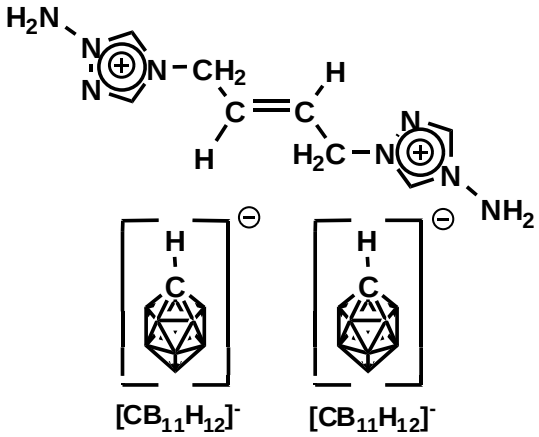
7

LIQUIFIES to a brown oil: 175.5 - 178.5 ºC



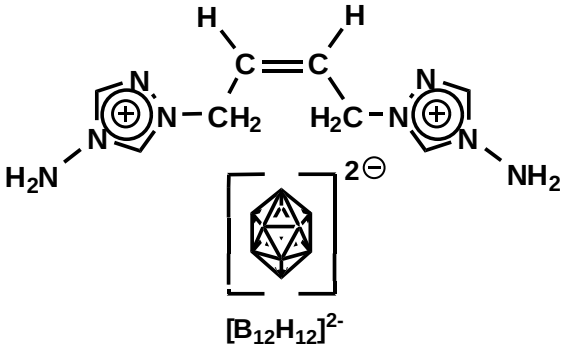
8

LIQUIFIES with rapid gas evolution:
237.8 - 239.6 ºC



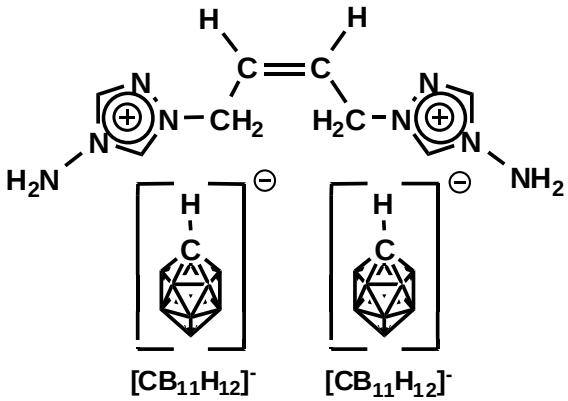
9

LIQUIFIES with gas evolution:
216.9 - 221.2 ºC



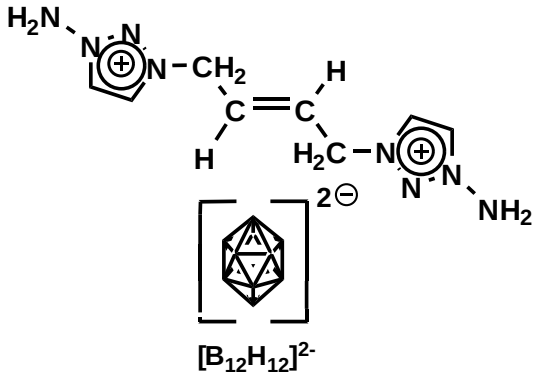
10

LIQUIFIES with gas evolution:
238.9 - 240.0 ºC



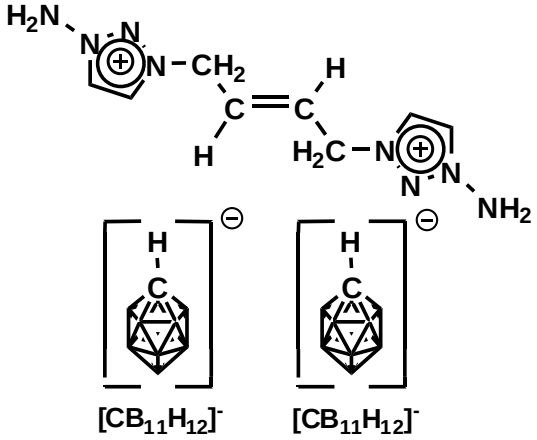
11

LIQUIFIES slowly to a brown oil:
170.0 - 174.0 °C



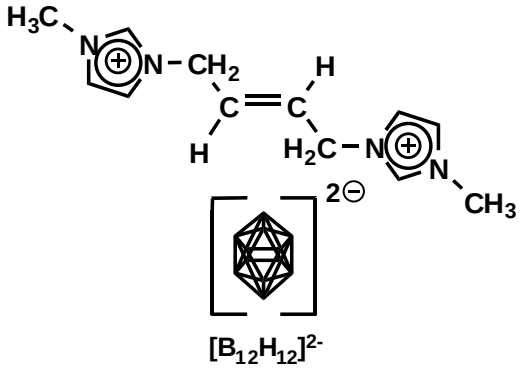
12

LIQUIFIES with rapid gas evolution:
229.7 - 230.6 °C



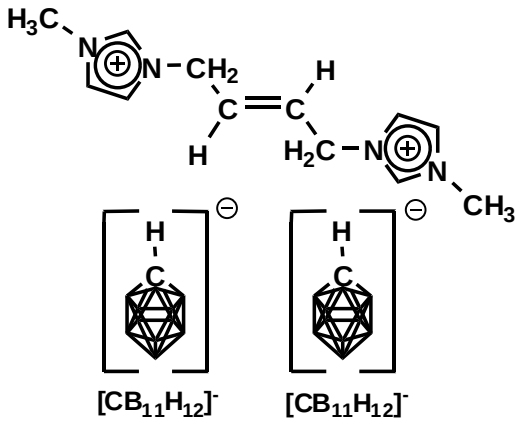
13

LIQUIFIES with rapid gas evolution:
206.2 - 208.6 °C



14

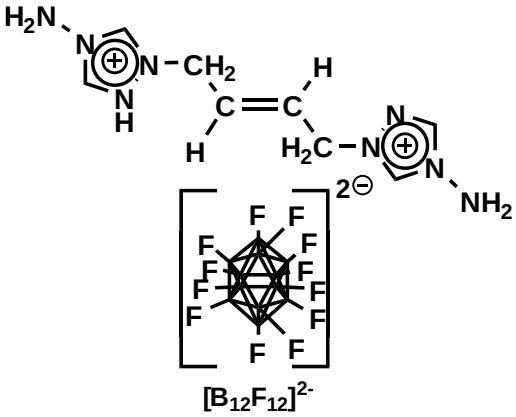
DECOMPOSITION in the solid state with very slow gas evolution to a brown residue: 305.1 - 398.0 °C



15

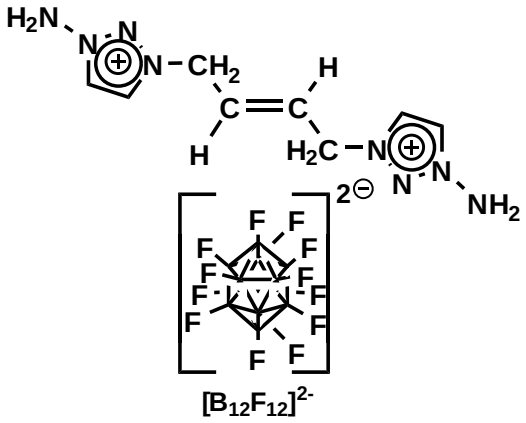
SOFTENS with possible morphology change: 210.1 - 231.4 °C

LIQUIFIES with slight oil discoloration: 251.9 - 255.2 °C



16 **(Large Scale Digested Sample)**

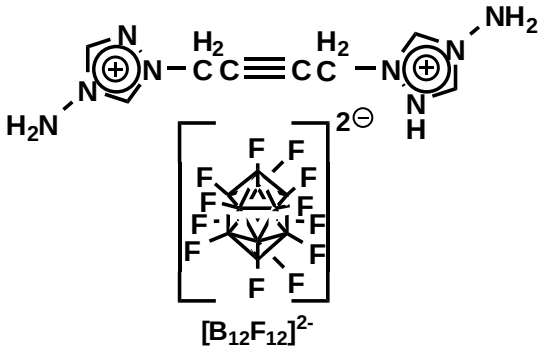
LIQUIFIES and darkens 302.8 - 303.4 °C with slow gas evolution noted at 303.6 °C



$[B_{12}F_{12}]^{2-}$

17 **(Small Scale Sample)**

LIQUIFIES and darkens with slow gas evolution: 237.6 - 239.6 ºC



$[B_{12}F_{12}]^{2-}$

18 **(Large Scale Digested Sample)**

LIQUIFIES and darkens to a dark brown oil with very slow gas evolution: 241.8 - 243.1 ºC

Ion Chromatography Cl^- or Br^- Analysis Results.

Each salt samples was weighed between 0.01 mg to 0 0.08 mg, and in one case 0.03 mg, into a plastic class B centrifuge tube and diluted to 25 mL using Type 1 ultra pure water. Samples that did not readily dissolve were heated to 80 °C with a plastic reflux cap. Each sample was passed through an IC Millex LG 0.2um syringe filter prior to injection. A three point calibration curve was generated using blank reagent water, 1 and 10 ppm NIST traceable Chloride and Bromide standards. Concentrations were determined by comparing peak area response of the samples to the standard calibration curve. Run detection limits displayed for each salt vary depending upon the sample mass used in each analysis. As can be seen from **Table 5** (page 23), the chloride ion content, from the residual KCl by-product, ranged from 0.3 to 0.5 weight percent, while the bromide content, from the residual KBr by-product (CsBr in the case of salt **18**), ranged from less than 0.04 weight percent to 0.83 weight percent.

Table 5. Ion Chromatography Residual Cl^- or Br^- Content in the Unsaturated Bridged Heterocyclium Di-Cation *closo*-Perfluoroborane, *closo*-Borane, and *closo*-Carborane Salts.

Bridged Salt Product[a]	**Run Detection Limit (wt. %)**	**Cl^- (wt. %)**	**Br^- (wt. %)**
6	0.08	---	< 0.08
7	0.08	---	0.10
8	0.08	---	0.28
9	0.08	---	< 0.08
10	0.03	0.03	---
11	0.03	0.05	---
12	0.08	---	< 0.08
13	0.07	---	< 0.07
14	0.08	---	0.33
15	0.08	---	0.83
16	0.04	---	< 0.04
17 (small scale)	0.12	---	< 0.12
18	0.08	---	< 0.08
16 (small scale)	0.10	---	0.50
18 (small scale)	0.08	---	< 0.08

[a]All bridged heterocyclium dication product salts were synthesized using either the potassium borane, carborane, or perfluoroborane reactant salt except for the small scale salt **18** sample where a cesium perfluoroborane reactant was used. Water solubility of the CsBr by-product salt is more than two times greater than that of the KBr by-product salt.[22]